Flexible polycaprolactone (PCL) supercapacitor based on reduced graphene oxide (rGO)/single-wall carbon nanotubes (SWNTs) composite electrodes

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Keywords

reduced, supercapacitor, (pcl), polycaprolactone, flexible, carbon, nanotubes, (swnts), composite, electrodes, oxide, (rgo)/single-wall, graphene

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Abstract

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Keywords: reduced graphene oxide (rGO)/single-wall carbon nanotubes (SWNTs) composite, polycaprolactone (PCL), spray coating technique, flexible supercapacitor.

1. Introduction

Recent studies on flexible devices have demonstrated a great deal of attention in a wide range of applications, such as *in vitro* diagnostics, robotics and advanced therapies [1-8]. These studies have employed electroactive materials on flexible substrates to achieve various functions, including high bendability or well-designed human-device interfaces [9-12]. Flexible energy storage devices like supercapacitors are essential components for fully implantable and flexible devices. In addition, to be generating electrical and mechanical function simultaneously, a variety of components involving graphene, hybrid composites or carbon nanotube assemblies need to integrated on flexible substrates [13-17] . Furthermore, flexible polymers should also be considered as a substrate to achieve flexible, implantable or wearable devices. Polycaprolactone (PCL) is a biodegradable, aliphatic polyester based polymer that has good resistance to solvents, water and oil. It also has unique chemical and mechanical properties resulting in its considerable commercial development for biomedical applications [18-21]. The addition of nanocarbon-based conducting materials like carbon nanotubes (CNTs) and graphene enables further possible applications, such as flexible supercapacitors.

Nanocarbon materials such as carbon nanotubes (CNTs) and graphene have been widely used as electrode materials in flexible supercapacitors due to their remarkable properties including excellent mechanical, electrical properties, large surface area, chemical stability and electrochemical properties [22-28]. Previous studies have demonstrated that nanocarbon based materials have potential for flexible supercapacitors. For this purpose, CNTs could be spray coated onto flexible substrates and used as an electrode [29-32]. Kaempgen *et al*. [29] have developed flexible, thin film supercapacitors based on the single-wall carbon nanotubes (SWNTs) spray-coated on poly (ethylene therephthalate) (PET) films. In order to fabricate fully printable devices, a polymer based solid state electrolyte was introduced as both a separator and electrolyte. The full device showed a specific capacitance of 36 F g^{-1}. Kang and co-workers [33] have reported low-cost and light weight flexible office paper and CNTs based supercapacitors with good chemical stability, high flexibility and large specific surface area. These exhibited 46.9 F g^{-1} of specific capacitance at 0.1 V s^{-1} of scan rate. Furthermore, it has excellent cycle stability with 0.5 % decrease of capacitance after 5000 charge/discharge cycles at a current density of 10 A g^{-1}.

Graphene also has been exploited as an electrode material, in particular for flexible supercapacitors [34-38]. The specific capacitance values from these graphene-based flexible supercapacitors ranged from 80 to 118 F g^{-1}, which are much lower than theoretical values (550 F g^{-1}) [39]. This is due to restacking of the graphene layers which decrease the electroactive area, resulting in lower capacitance values. In order to overcome this limitation, the CNTs can assist in separating graphene sheets and improving electroactive area [40]. CNTs are able to maintain graphene's high surface area and provide conductive pathways for efficient electron and ion transport [41-44]. For instance, Gao *et al*. [45] have developed a free-standing CNTs/graphene composite paper which was prepared by filtration method. It obtained a specific capacitance of 99.7 to 212.9 and 302 F g^{-1} when the mass ratio of the CNTs increased from 0 to 20 % and 40 %, respectively. Although there has been a great deal of investigation on CNTs, graphene and CNTs/graphene composite bases supercapacitors, there use in flexible supercapacitors has been explored to a much lesser extent.

In this report, we have investigated flexible supercapacitors with high durability and flexibility based on CNTs/graphene composites. To fabricate the fully flexible devices, the CNTs/graphene composite electrodes on gold-coated polycaprolactone (PCL) substrate were prepared using a Flexicoat industrial automatic spray coating system from Sono-Tek (USA) and by assembling two electrodes with polymer based electrolyte (PVA-H_3PO_4) in a sandwich configuration. This electrolyte was used as it is readily available and has appropriate mechanical properties. Although it is not cytocompatible [46, 47].

In order to assess the practical and realistic electrochemical performance of the flexible supercapacitors, all of the electrochemical properties were characterized on a two-electrode system under various bending angles and bend/release cycles.

2. Experimental

2.1 Materials

Ammonia solution in water (28%) was from labtech and used as received. Single-wall carbon nanotubes (SWNTs) were obtained from Carbon Nanotechnologies, Inc (Houston, TX) and used as an electrode material. Graphite powder was purchased from Bay Carbon. Milli-Q water with a resistivity of 18.2 mΩ cm^{-1} was used in all preparations. Potassium permanganate, hydrazine hydrate, phosphorous pentaoxide, triethylamine, concentrate nitric acid (70%) and N, N-Dimethylformamide (DMF) were sourced from Sigma-Aldrich and used as received. Polyvinyl alcohol (PVA, Mw = 124,000-186,000 g mol^{-1}) and polycaprolactone (PCL) (Mw = 80,000) were obtained from Sigma-Aldrich. Orthophosphoric acid (H_3PO_4) (85%) was purchased from Ajax Finechemicals.

2.2 Preparation of stretchable polymer electrolyte

Stretchable polymer electrolyte is fabricated by solvent casting method. Polyvinyl alcohol (PVA) (1g) was dissolved in Milli-Q water (10 mL) at 90 ℃ under vigorous stirring until the solution became clear, then orthophosphoric acid (H_3PO_4) (1.5g) is added into the PVA solution and stirred at room temperature overnight. The viscous PVA/H_3PO_4 solution was used as a stretchable electrolyte and separator to fabricate polycaprolactone (PCL) full devices.

2.3 Fabrication of flexible rGO/SWNTs composite electrode

In order to prepare flexible polycaprolactone (PCL) substrates, the pellet type of PCL was hot pressed at 90 ℃ to obtain approximately 0.5 mm thick films. The film was then cut to strips with a length of 5 cm and a width of 1 cm. After cutting the film, a 150 nm thick layer of gold was coated onto the PCL film by sputter coating (Edwards Sputter Coater AUTO306, BOC Ltd, United Kingdom), enabling it to be used as a current collector. The PCL film (1cm x 5cm x 0.5 mm) was transferred to a glass microscope slide, and then held using adhesive tape. The PCL film/slide assembly was fixed horizontally to the centre of the hotplate in the spray coating instrument. Once the hotplate is stabilized at 40°C, rGO/SWNTs dispersions were spray coated onto the PCL using a Sono-Tek Flexicoat industrial spray coating system (USA) with a 60 kHz Accumist nozzle and the dispersion feed rate of approximately 0.15 mL/min. Spraying is performed automatically at a distance of 15 cm from the PCL substrate. Many thin coats are applied, allowing a few seconds for drying between coats, until the entire 10 mL suspension is exhausted. After spray coating, the rGO/SWNTs composite electrodes were dried in a vacuum oven at room temperature overnight to evaporate residual solvent.

2.4 Preparation of flexible Polycaprolactone (PCL) supercapacitor

The flexible PCL supercapacitor was fabricated by assembling the flexible rGO/SWNTs composite electrodes and polymer (PVA-H_3PO_4) electrolyte in a sandwich conformation (Figure 1a and b). Copper tapes were attached at the edge of gold coated substrate for electrical contacts (Figure 1a). The PVA/H_3PO_4 solution was heated to 50 ℃ then the fabricated rGO/SWNTs composite electrodes were soaked in the solution for 10 min to diffuse electrolyte into the rGO/SWNTs composite film, then the electrodes were placed into a fume hood for 4 hrs to remove most of the water. Two such flexible rGO/SWNTs composite electrodes with PVA/H_3PO_4 electrolyte were pressed together face-to-face to form a sandwich configuration. The whole device was dried at room temperature overnight prior to further measurements. The surface morphology of the rGO/SWNTs composite film on the PCL substrate showed very rough and porous structure which is desirable for maximizing surface area (Figure 1c). The thickness of the polymer-based electrolyte between the two rGO/SWNTs composite electrodes was approximately 150 μm and whole device has approximately 1 mm thickness (Figure 1d). All of the electrochemical properties for the flexible PCL supercapacitor were carried out on a two-electrode configuration under fixed 180^o, 120^o, 60^o, 30^o of bending angle and 0 to 500 bending/release cycles at 30^o bending angle using a Shimadzu EZ mechanical tester. In order to achieve the reproducibility of the PCL supercapacitor, we assessed the specific capacitance of 10 devices.

3. Characterization

3.1 Cyclic Voltammetry

Cyclic Voltammetry (CV) measurements were performed at room temperature with a two electrode system using an electrochemical analyzer (EDAQ Australia) and EChem V2 software (ADI Instruments Pty. Ltd). CV measurements were recorded over the scan rate range 5 ~ 100 mV s^{-1}. All of the electrodes had bend and release cycles applied at a speed of 50% s^{-1} using a Shimadzu EZ mechanical tester.

3.2 Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) was used to probe the electrical double layer effects at the electrode/electrolyte interface. EIS measurements were performed at room temperature using a Gamry EIS 3000^{TM} system (Gamry, USA) where the frequency range spanned 100 kHz to 0.01 Hz with an amplitude of 10mV (rms) at open circuit potential.

3.3 Charge and discharge measurement

Galvanostatic charge–discharge tests of the flexible PCL supercapacitor were performed using a battery test system (Neware electronic Co.) between 0 V and 0.8 V with constant current density as 1 A g^{-1}.

4. Results and Discussion:

Cyclic voltammetry (CV) was used to perform electrochemical behavior under different bending angle conditions (Figure 2a). The flexible PCL supercapacitor showed rectangular CV responses even at 30^{o} of bending angle (Figure 2a), indicating that is highly reversible charge-discharge processes. The bending of the flexible PCL supercapacitor has no effect on the capacitive behavior. It could be bent to 30^{o} without degrading electrochemical performance.

The flexible PCL supercapacitor was also characterized by electrochemical impedance spectroscopy (EIS) under different bending conditions to obtain the electrochemical interfacial properties (Figure 2b). Nyquist plots exhibited a line close to 90º at low frequency even at an acute angle (30^{o}) conditions, indicating a resonable capacitive behavior (Figure 2b) [48, 49]. The internal resistance was 4.8 ohms at the unbent state (180^{o}) and increased to 5.4

ohms at 30º bending state (Figure 2b). There was no significant change in the internal resistance under different bending conditions.

Galvanostatic charge/discharge curves under different bending conditions with a constant current density of 1 A g^{-1} are illustrated in Figure 3a. The charge/discharge curves demonstrated high electrochemical performance under various bending conditions without *iR* drop. The symmetrical shape of the curves indicated that highly conductive rGO/SWNTs composites offer a bridge for the transfer of ions and electrons, thus decreasing internal resistance (Figure 3a). The average specific capacitance of the flexible PCL supercapacitor at 180^{o} of bending condition was 52.5 ± 0.4 (mean ± S.D., n = 10 devices) F g^{-1}, which maintained under 120º, 60º and 30º bending conditions, respectively (Figure 3b). These results agree with the surface resistance of the rGO/SWNTs composite film on the PCL substrate under the same condition (Figure 3c). The cycling stability under different bending conditions during 1000 charge/discharge cycles with constant current density of 1 A g^{-1} is given in Figure 3d. The flexible PCL supercapacitor still retained ≈ 99 % of its initial capacitance (52.5 F g^{-1}) with application of 4000 charge/discharge cycles, demonstrating high endurability. For these measurements, 1000 charge/discharge cycles are performed at 180^{o}, 120º, 60º and 30º bending conditions. The high stability can be attributed to the flexible electrodes in addition to the interpenetrating network structure between the rGO/SWNTs composite electrodes and PVA-H_3PO_4 gelled electrolyte. The solidification of the electrolyte during the fabrication of device was able to act like a glue holding all of the components together and enhancing the mechanical integrity and stability even under extreme bending conditions [36].

Cyclic Voltammetry (CV) measurements were carried out to investigate the electrochemical properties as a function of bending cycle. The CV responses after 0 to 500 bending cycles at

30^o with a scan rate of 100 mV s^{-1} are presented in Figure 4a. A slightly reduced current was observed after numerous bending cycles, which might be attributed to the inclusion/ejection and diffusion of counter ions being slow compared to the transfer of electrons in the rGO/SWNTs film [23, 50]. Importantly, the CV curve after 500 bending cycles still maintained a rectangular shape, indicating the charge / discharge responses of the flexible PCL supercapacitor.

Nyquist plots exhibited characteristic capacitive behaviour and electrochemical interfacial properties after 0 to 500 bending cycles (Figure 4b). In the high frequency regime (Figure 4b inset), it can be seen that the semi-circles regime increased with respect to increase in number of bending cycles. This is attributed to an increase in contact impedance between the rGO/SWNTs composite film and gold current collector as well as electrolyte resistance within the pores of the rGO/SWNTs composite film [51]. The internal resistance of the unbent PCL supercapacitor was 4.3 Ω, which increased to 5.8 Ω, 7 Ω, 7.2 Ω, 8.5 Ω and 9.6 Ω after 100, 200, 300, 400 and 500 bending cycles, respectively (Figure 4b). It was likely due to the low electrical conductivity on the rGO/SWNTs composite film after prolonged bending cycles (Figure 4c).

Galvanostatic charge/discharge curves as a function of bending cycle (Figure 5a) was demonstrated with a constant current density of 1 A g^{-1}. The charge/discharge curves presented good capacitive behavior and symmetrical shape without *iR* drop even after prolonged bending cycles up to 500 [52], indicating that the highly conductive rGO/SWNTs composite electrode creates a pathway for the transfer of ions and electrons with reducing internal resistance [53]. The average specific capacitance value of the unbent PCL supercapacitor was 52.5 ± 0.6 (mean ± S.D., n = 10 devices) F g^{-1} and decreased to 37.5 ± 0.5 (mean ± S.D., n = 10 devices) F g^{-1} after 500 bending cycles (Figure 5b). This result also agree with the high surface resistance of the rGO/SWNTs composite film on the PCL substrate after repetitive bending cycle up to 500 (Figure 4c).

The cycling stability of the PCL supercapacitor when subjected to a different number of bending cycles (Figure 5d) demonstrated typical galvanostatic charge/discharge profiles with a constant current density of 1 A g^{-1}. The specific capacitance retained 65% its initial capacitance (52.5 F g^{-1}) after 500 bending cycles with application of 6000 charge/discharge cycles (Figure 5c and d). The capacitance value might be due to the high resistance induced by the cracks on the rGO/SWNTs film after bending cycle [36]. The cracks also cause irreversible loss of junctions between electrode and electrolyte [54].

5. Conclusion

In this report, we have fabricated a flexible polycaprolactone (PCL) supercapacitor based on the rGO/SWNTs composite electrode with polymer electrolyte (PVA-H_3PO_4). Bending of the PCL device has almost no effect on the capacitive behaviour. The specific capacitance (unbent state) was 52.5 F g^{-1}, which was retained at the 120º, 60º and 30º bending conditions, respectively. However, the specific capacitance (unbent state) decreased to 37.5 F g^{-1} after 500 bending cycles. The specific capacitance of PCL supercapacitor retained 65% its initial capacitance after 500 bending cycle at 30^o bending angle with application of 6000 charge/discharge cycle. Moreover, the stability of the PCL supercapacitor was carried out via a charge/discharge test while in the bent state. Interestingly, the PCL supercapacitor showed only ~1% decrease in the capacitance under 180^o, 120º, 60º and 30º bending conditions with application of 4000 charge/discharge cycles (1000 cycles were applied at each bending condition), demonstrating high durability and flexibility. This was attributed to the highly flexible rGO/SWNTs composite electrodes along with the interpenetrating network structure between the electrodes and the PVA-H_3PO_4 gelled electrolyte.

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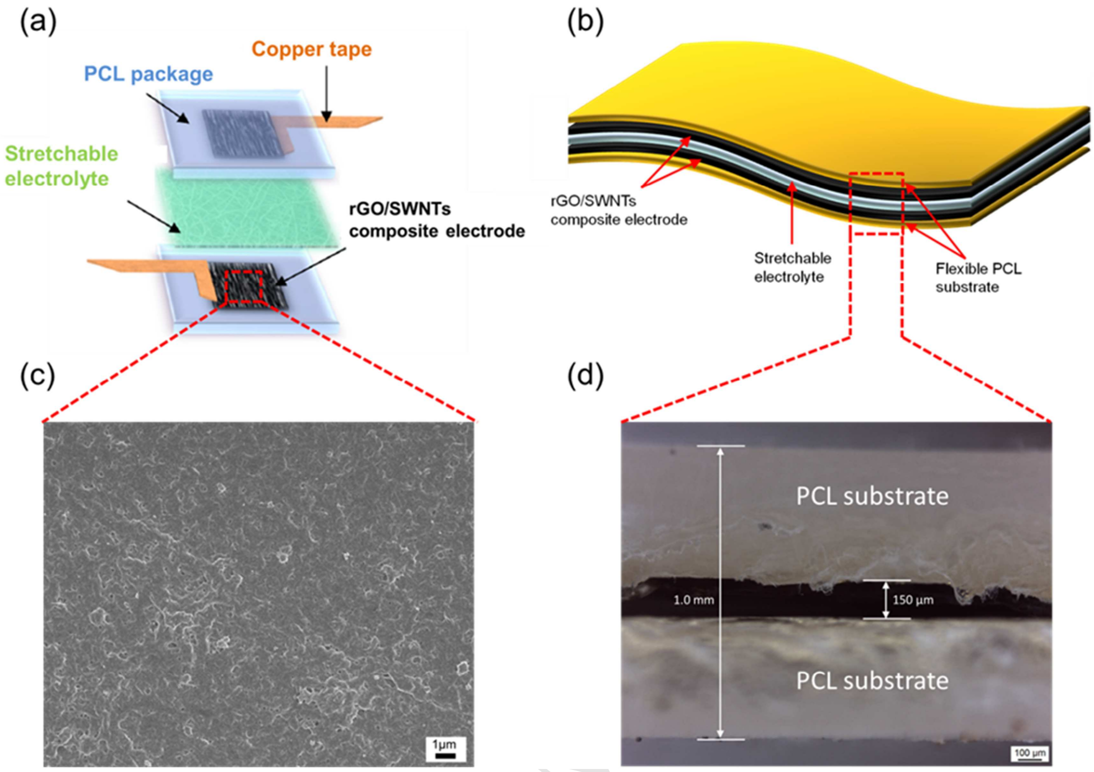

(a)
Copper tape
PCL package
Stretchable electrolyte
rGO/SWNTs composite electrode
(b)
rGO/SWNTs composite electrode
Stretchable electrolyte
Flexible PCL substrate
(c)
1μm
(d)
PCL substrate
1.0 mm
150 μm
PCL substrate
100 μm

Figure 1

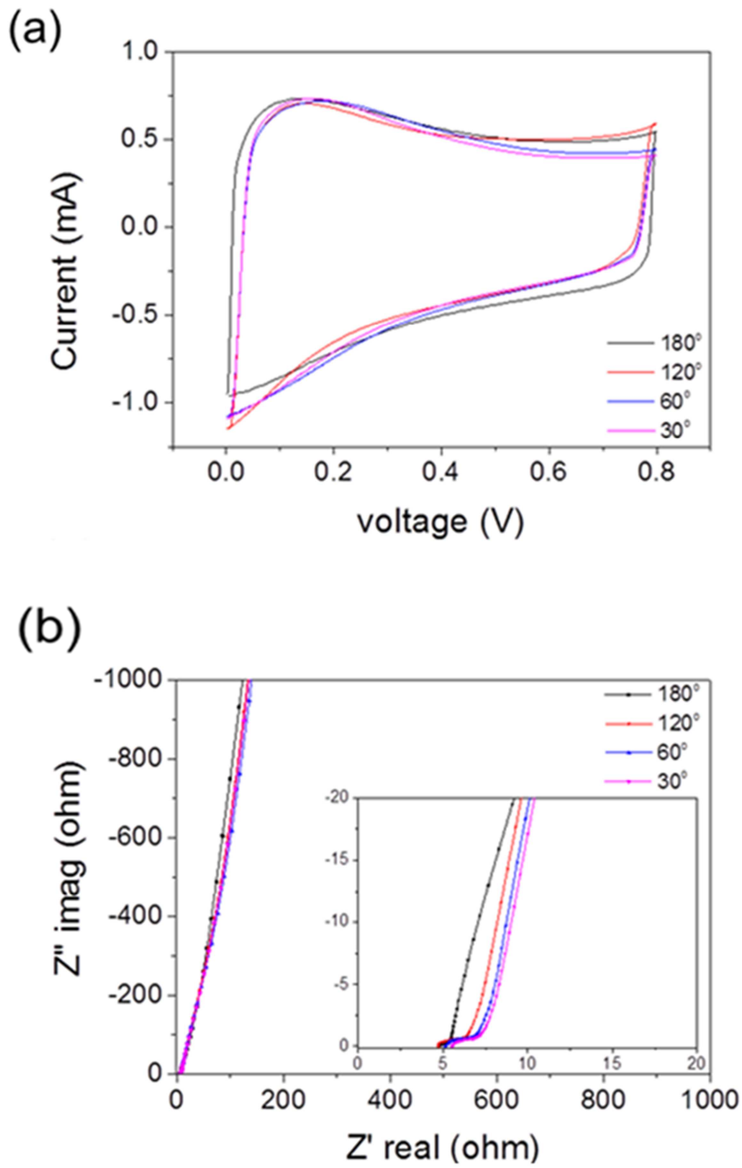
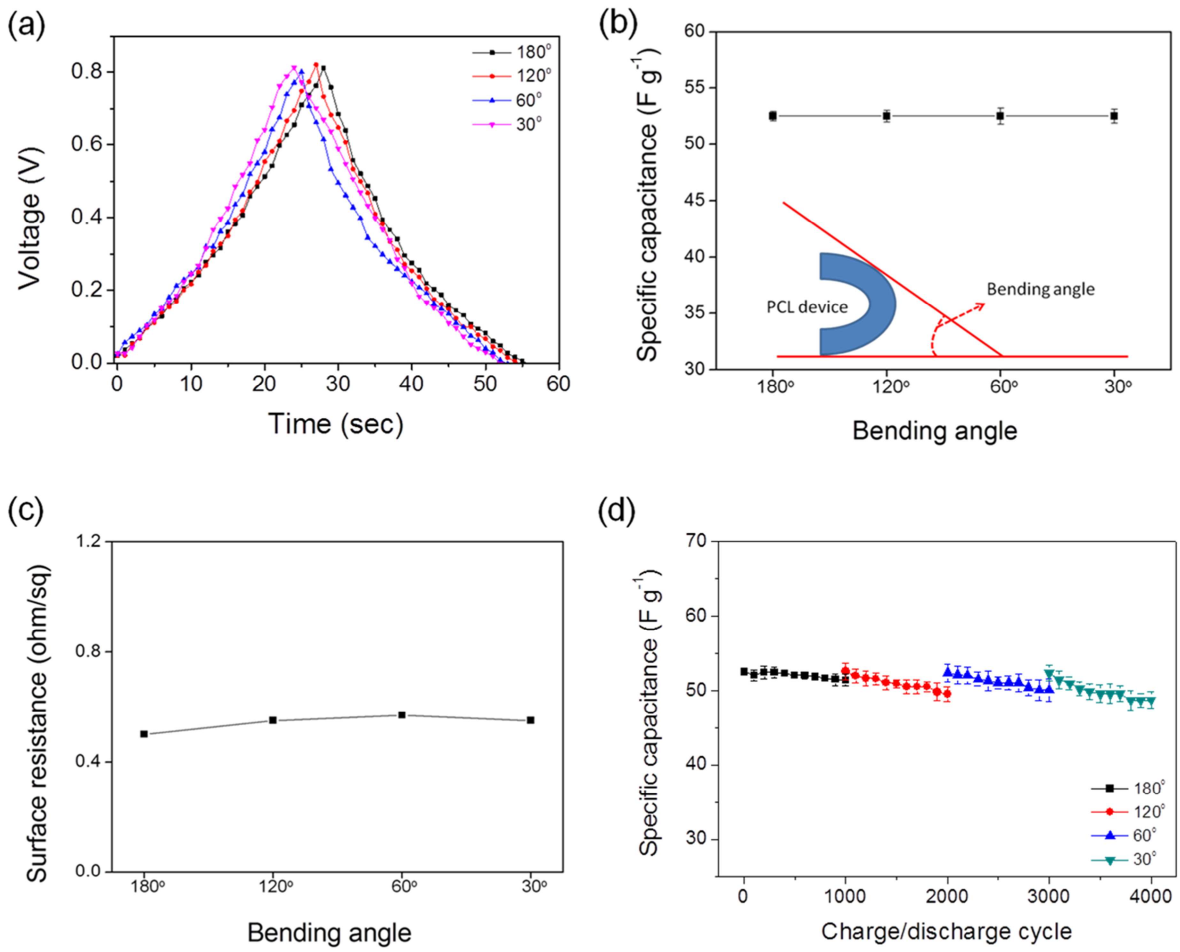

(a)
1.0
0.5
0.0
-0.5
-1.0
Current (mA)
0.0
0.2
0.4
0.6
0.8
voltage (V)
180°
120°
60°
30°
(b)
-1000
-800
-600
-400
-200
0
Z'' imag (ohm)
0
200
400
600
800
1000
Z' real (ohm)
180°
120°
60°
30°
-20
-15
-10
-5
0
0
5
10
15
20

Figure 2



(a)
Voltage (V)
Time (sec)
180°
120°
60°
30°
(b)
Specific capacitance (F g-1)
Bending angle
PCL device
Bending angle
180°
120°
60°
30°
(c)
Surface resistance (ohm/sq)
Bending angle
(d)
Specific capacitance (F g-1)
Charge/discharge cycle

Figure 3

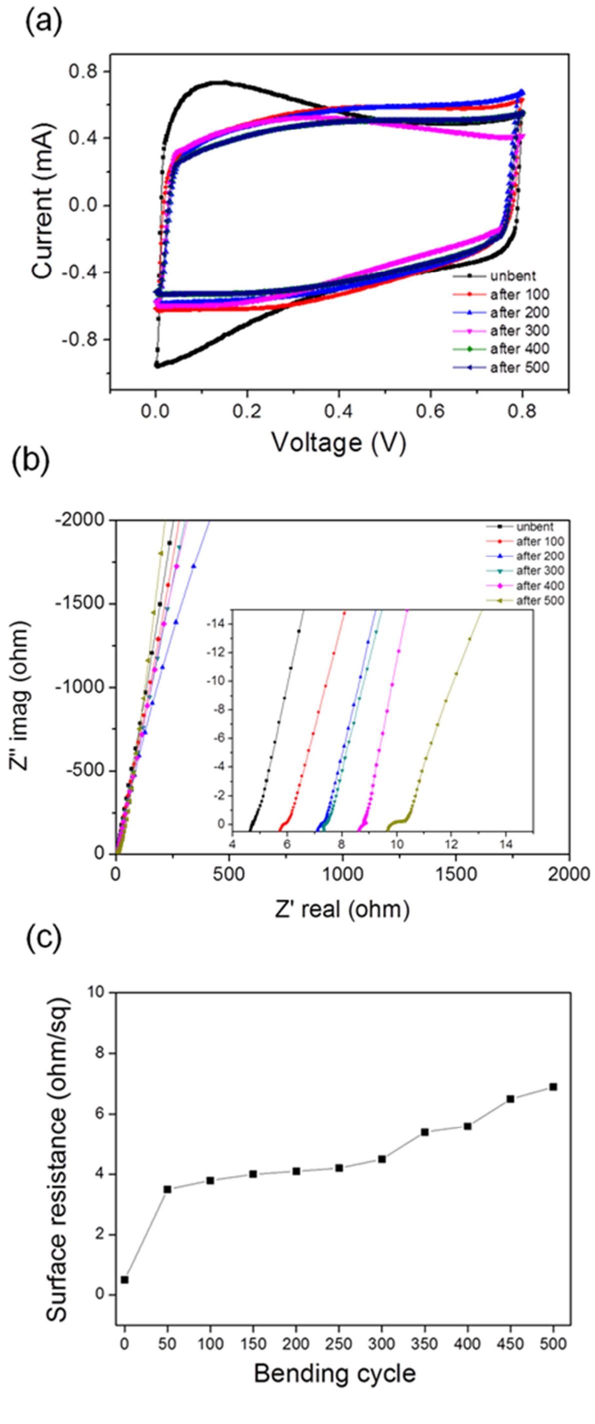

(a)
Current (mA)
Voltage (V)
unbent
after 100
after 200
after 300
after 400
after 500
(b)
Z'' imag (ohm)
Z' real (ohm)
unbent
after 100
after 200
after 300
after 400
after 500
(c)
Surface resistance (ohm/sq)
Bending cycle

Figure 4

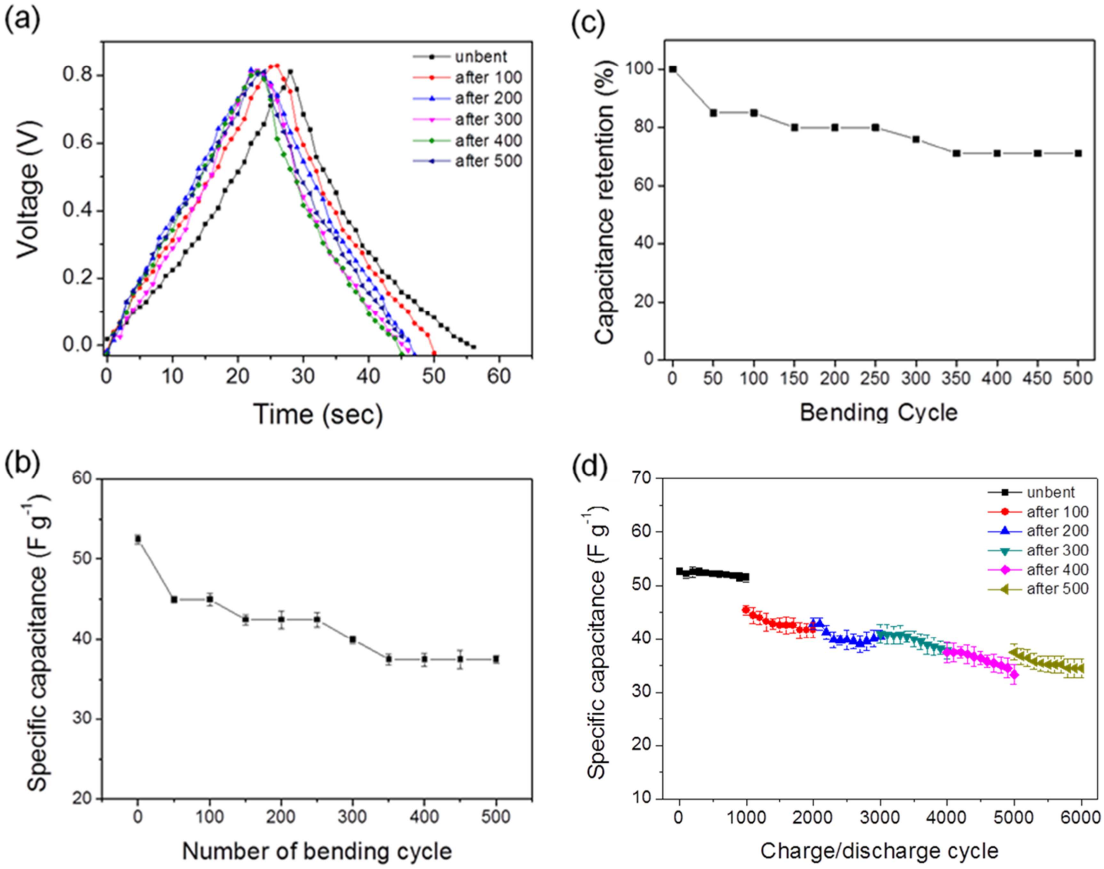

(a)
Voltage (V)
Time (sec)
unbent
after 100
after 200
after 300
after 400
after 500
(c)
Capacitance retention (%)
Bending Cycle
(b)
Specific capacitance (F g-1)
Number of bending cycle
(d)
Specific capacitance (F g-1)
Charge/discharge cycle
unbent
after 100
after 200
after 300
after 400
after 500

Figure 5

Captions

Figure 1: (a) and (b) Schematic of the main components for the flexible polycaprolactone (PCL) supercapacitor, (c) Surface morphology of the rGO/SWNTs composite film on the PCL substrate, (d) Optical microscopy image (cross section) of the PCL whole device.

Figure 2: Electrochemical properties of the flexible and biocompatible Polycaprolactone (PCL) supercapacitor under different bending condition (180º to 30º); (a) CV of the PCL supercapacitor under different bending condition at 100 mV s^{-1}. (b) Nyquist plots of the PCL supercapacitor under different bending condition with 0.01 Hz ~100 KHz frequencies.

Figure 3: Electrochemical properties of the flexible and biocompatible Polycaprolactone (PCL) supercapacitor under different bending condition (180º to 30º); (a) Charge/discharge test of the PCL supercapacitor under different bending condition with 1 A g^{-1} constant current density. (b) Specific capacitance of the PCL supercapacitor under different bending condition. (c) Surface resistance of the rGO/SWNTs composite film on the PCL under different bending condition. (d) Cycling stability of the PCL supercapacitor under different bending condition.

Figure 4: Electrochemical properties of the flexible and biocompatible Polycaprolactone (PCL) supercapacitor as a function of bending cycle (0 to 500 bending cycles); (a) CV of the PCL supercapacitor at different bending cycles with 100 mV s^{-1} of scan rate. (b) Nyquist plots of the PCL supercapacitor at different bending cycle with 0.01Hz ~ 100 KHz frequencies. (c) Surface resistance of the rGO/SWNTs composite film on the PCL substrate at different bending cycles.

Figure 5: Electrochemical properties of the flexible and biocompatible Polycaprolactone (PCL) supercapacitor as a function of bending cycle (0 to 500 bending cycles); (a)

Charge/discharge curves of the PCL supercapacitor with application of different bending cycle at 1 A g^{-1} current density. (b) Specific capacitance of the PCL supercapacitor with application of different bending cycle. (c) Capacitance retention of the PCL supercapacitor at different bending cycle. (d) Stability test of the PCL supercapacitor by charge/discharge measurement with application of different bending cycle at 1 A g^{-1} of current density.

1. Spray coating was conducted for flexible polycaprolactone(PCL) supercapacitor.
2. The highest capacitance value of the unbent PCL supercapacitor is 52.5 F g^{-1}.
3. PCL supercapacitor showed high durability through electrochemical measurements.